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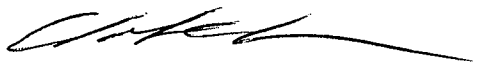
Signed this 29th day of February 2008



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Agent for colouring keratin materials, containing at least two components, and colouring processes

The present invention relates generally to an agent for colouring keratin materials, containing at least two components, in particular for colouring human skin and/or keratin fibres, and to various colouring processes using it.

In the field of colouring human keratin materials such as the skin, the hair, the eyelashes, the eyebrows and body hair, enzymatic catalysts are used at the present time to activate the coloration of dye precursors. Thus, the coloration of polyphenols is activated by oxidation in the presence of natural polyphenol oxidase. By way of example, catechin, in the presence of natural polyphenol oxidase, gives an orange-yellow coloration and dihydroxyphenylalanines (L-DOPA) give melanin. The main advantage of these enzymatic catalysts consists in producing pigments with novel colours and shades, without using oxidizing compounds. However, the major drawback of this colouring process is the use of enzymes, for which the toxicological risks, the stability in compositions, the reproducibility, the price and the immobilization often required are factors that greatly limit their uses.

Moreover, these catalysts are of protein nature and the use of proteins is not without risk for

cosmetological or dermatological use, especially on account of sensitization reactions.

The use of enzymatic catalysts in cosmetic preparations such as self-tanning products does not always allow a uniform coloration of the skin. Applying compositions containing dihydroxyacetone (or DHA), which is typically used in this type of application, to the whole body is long and tedious, and it is difficult to obtain a uniform coloration.

In the field of tanning and self-tanning creams, an improvement has been obtained by using chemical catalysts instead of enzymatic catalysts. Thus, patent application WO 92/20321 A describes a cream that promotes the tanning of fair skin when exposed to sunlight or to UVB rays, the composition of which comprises a physiologically acceptable medium and a pseudocatalase. The pseudocatalase is a coordination complex of a transition metal, the metal of which is Cu(I), Fe(II) or Mn(II) and the ligand of which is bicarbonate. The term "pseudocatalase" means a physiologically acceptable compound that catalyses the dismutation of H_2O_2 in vivo in a manner analogous to a catalase.

To treat skin depigmentation associated with blockages of the conversion of tyrosine to melanin, for instance vitiligo, patent application WO 92/20354

describes a composition containing a pseudocatalase in a physiologically acceptable medium.

This pseudocatalase is a coordination complex of Fe(II), Cu(I) or Mn(II), the ligand being bicarbonate.

The article by K. Schallreuter ("Pseudocatalase is a bis-manganese III-EDTA-$(HCO_3)_2$ complex activated by UVB or natural sun; J Investing Dermator Symp Proc 1999 Sep; 451; 91-6) mentions the use of a mixture of sodium hydrogen carbonate and manganese that has pseudocatalase activity, for the treatment of vitiligo. However, there is no indication concerning the coloration in any of these documents. Moreover, this composition contains a chelating agent that is EDTA.

In the field of colouring the hair, European patent EP 621 029 describes a composition comprising sodium chlorite, a water-soluble Fe, Mn or Cu salt, or a chelate of this salt, and an oxidation dye precursor.

Colouring the hair requires the use of H_2O_2-ammonium or amine combinations.

A process for intensifying the natural tanning of the skin is also known in patent US 6 399 046, this process consisting in stimulating melanogenesis in situ with polyphenols of the type such as catechin, catechin gallic ester or plant extracts

containing catechin or a catechin gallic ester, in particular extracts of green tea leaf. This process does not afford direct and fast coloration on the skin and the presence melanocytes is necessary.

There is thus a need to find novel compositions for colouring keratin materials, in particular for colouring the skin and/or keratin fibres, which does not require the use of enzymatic systems.

It was discovered in patent application FR 2 814943 that it is possible to achieve this aim by using a colouring agent (A) comprising at least one dye precursor chosen from compounds comprising at least one aromatic ring containing at least two hydroxyl groups (OH) borne by two consecutive carbon atoms of the aromatic ring, capable of becoming coloured, in the presence of oxygen, via oxidation by means of a purely chemical catalytic system comprising a first constituent chosen from Mn(II) and/or Zn(II) salts and oxides, and mixtures thereof, and a second constituent chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof. The said chemical catalytic system behaves like a pseudo-oxidase capable of imitating the oxidase activity without the drawbacks associated with the use of an enzymatic system.

However, the Applicant has found, firstly, that the persistence over time, the intensity and the uniformity of the colours obtained with this type of colouring agent (A) could be further improved. Secondly, this type of process does not allow sufficient control of the coloration reaction on the hair or the skin and cannot produce a wide range of shades that are more or less intense depending on the needs of the user and especially at different times of the day or over a period of several days.

The Applicant has discovered, surprisingly, that by applying to the keratin support to be coloured a second acidic composition (B) after the application of the colouring agent (A) as defined above, the colouring reaction revealed by the said agent (A) is stopped. Via a mordanting phenomenon, the acidic composition (B) allows the tannins thus formed to be fixed onto the proteins of the keratin materials. The application of the acidic composition (B) makes it possible, unexpectedly, firstly to reinforce the fastness of the colour over time and secondly to control the coloration reaction on the keratin support by stopping it until the shade desired by the user is obtained.

The Applicant has also discovered, surprisingly, that by applying an alkaline composition

(C) after the application of the colouring agent (A) as defined above and optionally after applying the acidic composition (B) defined above, the colour obtained in the preceding step can be revived by increasing its intensity; the new shade obtained can again be controlled by stopping the reaction at the chosen moment by applying the said second composition (B).

This process of colouring, fixing and/or reviving the colour may be repeated as many times as necessary, over a period of several days.

One subject of the present invention is thus an agent for colouring keratin materials, containing at least two components, characterized in that it comprises:

(i) a first component (A) by itself or including two components (A_1) and (A_2) comprising, in a physiologically acceptable medium, at least one dye precursor chosen from compounds comprising at least one aromatic ring containing at least two hydroxyl groups borne by two successive carbon atoms of the aromatic ring, and at least one catalytic system comprising a first catalyst (1) chosen from Mn(II) and/or Zn(II) salts and oxides, and mixtures thereof, and a second catalyst (2) chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof; the catalysts (1) and

(2) possibly being present in a single constituent or separated into two components (A_1) and (A_2);

(ii) a component (B) comprising an acidic composition, and/or

(iii) a component (C) comprising an alkaline composition.

The invention also relates to various processes for colouring keratin materials using the said colouring agent.

Finally, the present invention relates to packaging and presentation forms for the various components of the colouring agent according to the invention.

The term "keratin materials" means natural textile fibres consisting of keratin, for instance cotton, silk, wool, and materials such as the skin, the scalp, the nails, the hair, body hair, the eyelashes and the eyebrows, and also mucous membranes.

In the colouring agent in accordance with the invention, the component (A) may be a single component or may include two components (A_1) and (A_2). It comprises at least one dye precursor chosen from compounds comprising at least one aromatic ring containing at least two hydroxyl groups borne by two consecutive carbon atoms of the aromatic ring and at least one catalytic system comprising a first catalyst

(1) chosen from Mn(II) and/or Zn(II) salts and oxides, and mixtures thereof, and a second catalyst (2) chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof; the catalysts (1) and (2) possibly being present in a single component or separated into two components (A_1) and (A_2).

According to one particular embodiment of the invention, the dye component (A) comprises two components (A_1) and (A_2) packaged separately, with: (A_1) comprising, in a physiologically acceptable medium, the said dye precursor and one of the catalysts (1) or (2) and (A_2) comprising, in a physiologically acceptable medium, the other catalyst (1) or (2).

The proportions of the first catalyst (1) and of the second catalyst (2) are preferably chosen such that:

$$\frac{[Mn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \neq 0$$

$$\frac{[Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Zn(II)] \neq 0$$

$$\frac{[Mn(II)+Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \text{ and } [Zn(II)] \neq 0$$

in which [Mn(II)], [Zn(II)] and [HCO_3] represent, respectively, the molar concentrations of Mn(II),

Zn(II) and HCO_3 in the composition.

Generally, the ratio $\frac{[Mn(II)]}{[HCO_3]}$ ranges from 10^{-5} to 10^{-1}, preferably from 10^{-3} to 10^{-2} and is typically about 5×10^{-3}.

In the case of Zn(II), the ratio $\frac{[Zn(II)]}{[HCO_3]}$ is generally from about 10 to 100 times greater than the ratio in the case of Mn(II).

Typically, this ratio is 10^{-4} or more, preferably 10^{-3} or more and preferentially about 5×10^{-1}.

In the case of a mixture of Mn(II) and Zn(II), the ratio generally ranges from 10^{-5} to 10^{-1} and preferably from 10^{-3} to 10^{-2}, this ratio being chosen higher when the proportion of Zn(II) in the mixture increases.

Generally, the molar concentration of Mn(II), Zn(II) or Mn(II) + Zn(II) in the final composition ranges from 10^{-3} to 10 mM/l and preferably from 10^{-2} to 1 mM/l.

When only one or more Mn(II) salts or oxides are used, the molar concentration of Mn(II) in the final composition is typically from 10^{-3} to 10^{-1} mM/l and preferably 10^{-2} to 10^{-1} mM/l.

Preferably, when only one or more Zn(II) salts or oxides are used, the concentration of Zn(II) in the final composition is from 5×10^{-2} to 10 mM/l and better still from 5×10^{-1} to 1 mM/l.

Among the Mn(II) and Zn(II) salts that are suitable for the present invention, mention may be made of the chloride, fluoride, iodide, sulfate, phosphate, nitrate and perchlorate, carboxylic acid salts, and mixtures thereof. They may be derived from a natural mineral water.

Examples that may be mentioned include manganese chloride, manganese carbonate (for example rhodochrosite), Mn(II) difluoride, Mn(II) acetate tetrahydrate, Mn(II) lactate trihydrate, Mn(II) phosphate, Mn(II) iodide, Mn(II) nitrate trihydrate, Mn(II) bromide, Mn(II) perchlorate tetrahydrate and Mn(II) sulfate monohydrate.

The salts that are particularly preferred are $MnCl_2$ and $ZnCl_2$.

The carboxylic acid salts also include hydroxylated carboxylic acid salts such as gluconate.

Among the alkali metal and alkaline-earth metal hydrogen carbonates that may be mentioned are Na, K, Mg, Ca hydrogen carbonate and mixtures thereof, preferably Na hydrogen carbonate. They may be derived from a natural mineral water.

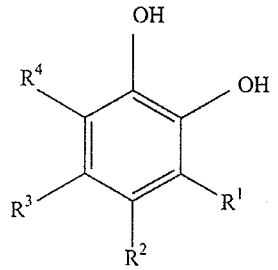
As mentioned previously, the chemical catalytic system according to the invention constitutes a pseudo-oxidase in that it oxidizes polyphenols, in

the presence of oxygen, as would a natural enzymatic catalyst having polyphenol oxidase activity.

The dye precursors of the compositions of the invention are compounds or mixtures of compounds comprising at least one aromatic ring, preferably a benzene ring, comprising at least two hydroxyl groups (OH) borne by two consecutive carbon atoms of the aromatic ring.

The aromatic ring may be a fused aromatic ring optionally containing one or more hetero atoms, such as naphthalene, tetrahydronaphthalene, indane, indene, anthracene, phenanthrene, indole, isoindole, indoline, isoindoline, benzofuran, dihydrobenzofuran, chroman, isochroman, chromene, isochromene, quinoline, tetrahydroquinoline and isoquinoline.

The dye precursors according to the invention may be represented by the formula:



(I)

in which the substituents R^1 to R^4, which may be identical or different, represent a hydrogen atom, a halogen, hydroxyl, carboxyl, alkylcarboxylate, optionally substituted amino, optionally substituted linear or branched alkyl, optionally substituted linear

or branched alkenyl, optionally substituted cycloalkyl, alkoxy, alkoxyalkyl or alkoxyaryl radical, the aryl group possibly being optionally substituted, an aryl or substituted aryl radical, an optionally substituted heterocyclic radical, or a radical containing one or more silicon atoms, in which two of the substituents R^1 to R^4 together form a saturated or unsaturated ring optionally containing one or more hetero atoms and optionally fused with one or more saturated or unsaturated rings optionally containing one or more hetero atoms.

The saturated or unsaturated, optionally fused rings may also be optionally substituted.

The alkyl radicals are generally C_1-C_{10} alkyl radicals and preferably C_1-C_6 alkyl radicals, such as methyl, ethyl, propyl, butyl, pentyl and hexyl.

The alkoxy radicals are generally C_1-C_{10} alkoxy radicals, such as methoxy, ethoxy, propoxy and butoxy.

The alkoxyalkyl radicals are preferably (C_1-C_{20})alkoxy(C_1-C_{20})alkyl radicals, such as methoxymethyl, ethoxymethyl, methoxyethyl, ethoxyethyl, etc.

The cycloalkyl radicals are generally C_4-C_8 cycloalkyl radicals, preferably cyclopentyl and cyclohexyl radicals. The cycloalkyl radicals may be

substituted cycloalkyl radicals, in particular substituted with alkyl, alkoxy, carboxylic acid, hydroxyl, amine and ketone groups.

The alkenyl radicals are preferably C_1-C_{20} radicals, such as ethylene, propylene, butylene, pentylene, methyl-2-propylene and decylene.

The radicals containing one or more silicon atoms are preferably polydimethylsiloxane, polydiphenylsiloxane, polydimethylphenylsiloxane and stearoxydimethicone radicals.

The heterocyclic radicals are generally radicals comprising one or more hetero atoms chosen from O, N and S, preferably O or N, optionally substituted with one or more alkyl, alkoxy, carboxylic acid, hydroxyl, amine or ketone groups.

Among the preferred heterocyclic radicals that may be mentioned are furyl, pyranyl, pyrrolyl, imidazolyl, pyrazolyl, pyridyl and thienyl groups.

More preferably, the heterocyclic groups are fused groups such as benzofuryl, chromenyl, xanthenyl, indolyl, isoindolyl, quinolyl, isoquinolyl, chromanyl, isochromanyl indolinyl, isoindolinyl, coumarinyl and isocoumarinyl groups, these groups possibly being substituted, in particular with one or more OH groups.

The preferred dye precursors are:

- flavanols such as catechin and epicatechin

gallate,

- flavonols such as quercetin,
- anthocyanidins such as peonidin,
- anthocyanins, for example oenin,
- hydroxybenzoates, for example gallic acid,
- flavones such as luteolin,
- iridoids such as oleuropein,

these products possibly being osylated (for example glucosylated) and/or in the form of oligomers (procyanidins);

- hydroxystilbenes, for example 3,3',4,5'-tetrahydroxystilbene, which are optionally osylated (for example glycosylated);
- 3,4-dihydroxyphenylalanine and its derivatives;
- 2,3-dihydroxyphenylalanine and its derivatives;
- 4,5-dihydroxyphenylalanine and its derivatives;
- 4,5-dihydroxyindole and its derivatives;
- 5,6-dihydroxyindole and its derivatives;
- 6,7-dihydroxyindole and its derivatives;
- 2,3-dihydroxyindole and its derivatives;
- dihydroxycinnamates such as caffeic acid and chlorogenic acid;
- hydroxycoumarins;
- hydroxyisocoumarins;
- hydroxycoumarones;
- hydroxyisocoumarones;

- hydroxychalcones;
- hydroxychromones;
- anthocyans;
- quinones;
- hydroxyxanthones; and
- mixtures thereof.

When the dye precursors have D and L forms, the two forms may be used in the compositions according to the invention.

By varying the nature of the various dye precursors and their proportions in the composition, the colour of the final dye composition may be varied. A range of colours is thus obtained.

The polymers formed in particular with catechin, gallic acid and derivatives thereof (tannins) have antimicrobial properties by trapping microorganisms during polymerization. These tannins also have astringent properties that are advantageous for the skin.

The dye precursors may be extracts of plants, of fruits, of citrus plants and of vegetables, and mixtures of these extracts, which contain many polyphenols as defined above.

Among the plant extracts that may be mentioned are extracts of rose, of sorghum and of tea.

Among the fruit extracts that may be

mentioned are extracts of apple, of grape (in particular of grapeseed), of cocoa (beans and/or pods) and of banana.

Among the vegetable extracts that may be mentioned is extract of potato.

It is also possible to use mixtures of plant and/or fruit extracts such as mixtures of extracts of apple and of tea and mixtures of extracts of grape and of apple.

Depending on the parts of the fruits used, for example grape pulp or seed, the coloration obtained is different.

The amount of dye precursor in the final composition should be sufficient to obtain a visible coloration. This amount may vary within a wide range depending on the nature of the precursor and the desired intensity for the coloration.

In general, a suitable coloration will be obtained when the amount of dye precursor is such that the content of dye precursor in the final component (A) is at least 10 micromol per millilitre of component (A).

The physiologically acceptable medium for the dye component (A) or of the components (A_1) and (A_2) is solid or liquid medium that does not harm the colouring property of the precursors or the catalytic effect of

the catalytic system. It is preferably a solubilizing medium for the dye precursor and has bacteriostatic properties.

Among the solvents for the precursors that are suitable for formulating the compositions according to the invention, mention may be made of water, alcohols and polar solvents, and mixtures thereof.

The alcohols are preferably lower (C_1-C_6) alkanols such as ethanol and isopropanol, and alkanediols such as ethylene glycol, propylene glycol and pentanediol.

Among the polar solvents that may be mentioned are ethers, esters (in particular acetates), dimethyl sulfoxide (DMSO), N-methylpyrrolidone (NMP) and ketones (in particular acetone), and mixtures thereof.

The physiologically acceptable medium preferably comprises water (in particular distilled or deionized water) or a water/alcohol mixture, in particular water/ethanol.

The amount of alcohol in the water/alcohol mixture may represent up to 80% by weight of the water/alcohol mixture, preferably 1% to 50% by weight and better still 5% to 20% by weight.

Preferably, the component (A) according to the invention is free of agent for chelating the Mn(II)

and/or Zn(II) salts used, since these agents tend to inhibit the oxidation of the dye precursors.

The solvents are preferably present in proportions preferably of between 1% and 40% by weight approximately relative to the total weight of the dye composition (A), and even preferably between 5% and 30% by weight approximately.

When it is intended for colouring the hair, the dye component (A) in the form of a single component or the two components (A_1) and (A_2) packaged separately may be in various forms, such as in the form of a lotion, a cream or a gel, or in any other form that is suitable for colouring keratin fibres, and especially human hair. It may also contain various adjuvants conventionally used in hair colouring compositions, such as anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, mineral or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, antioxidants, penetrating agents, fragrances, buffers, dispersants, conditioners, for instance volatile or non-volatile, modified or unmodified silicones, film-forming agents, ceramides, opacifiers and propellants.

When it is intended for colouring the skin,

the dye component (A) in the form of a single component or the two components (A_1) and (A_2) packaged separately may be in the form of a cream or a milk, or in the form of a gel or a cream-gel, a lotion, a powder or a solid, or in any other form that is suitable for colouring the skin. It may also contain various adjuvants conventionally used in skin colouring compositions, such as fatty substances, organic solvents, anionic, cationic, nonionic, amphoteric or zwitterionic surfactants or mixtures thereof, anionic, cationic, nonionic, amphoteric or zwitterionic polymers or mixtures thereof, mineral or organic thickeners, and in particular anionic, cationic, nonionic and amphoteric polymeric associative thickeners, softeners, antioxidants, free-radical scavengers, opacifiers, emollients, silicones, antifoams, moisturizers, vitamins, insect repellants, fragrances, surfactants, anti-inflammatory agents, substance P antagonists, fillers, propellants, dyes, and organic or mineral sunscreens.

The component (A) in the form of a single component or the two components (A_1) and (A_2), independently of each another, may be packaged in various forms, for instance in the form of an airtight metal tube, a sachet, a sealed wipe, an ampule, an aersol, a spray or a solid block, or any other

packaging form that is suitable for colouring the chosen keratin support.

According to a first embodiment, the component (A) according to the invention may be packaged in a one-compartment device containing the dye precursor(s) and the catalystic system.

This device may be, for example, an airtight metal tube; a sachet; a sealed wipe; an ampule; an aerosol containing one or more standard inert propellent gases chosen from nitrogen, saturated hydrocarbons such as butane, propane or isopropane, and fluorohydrocarbons, for instance Freon®; a spray equipped with a pump without air intake; a solid block such as a bead for the bath.

In a second embodiment, the component (A) according to the invention may be packaged in the form of a kit comprising two separate containers containing, respectively, the components (A_1) and (A_2) as defined above, the components (A_1) and (A_2) being mixed together or applied successively at the time of use.

Each of the two containers, independently of each other, may be packaged, for example, in the form of an airtight tube, a sachet, a sealed wipe, an ampule, an aerosol, a spray equipped with a pump without air intake, or a solid block such as a bath bead, or any other packaging form that is suitable for

colouring the chosen keratin support.

A two-compartment aerosol device containing, respectively, the components (A_1) and (A_2) and with which a distribution orifice may be selectively placed in communication may also be envisaged; depending on the configuration of the device, the components (A_1) and (A_2) may be distributed simultaneously or successively at the time of use.

A system containing two compartments each equipped with a pump without air intake, the first compartment containing the component (A_1) with the dye precursor(s) and one of the catalysts (1) or (2) as defined above, and the other compartment containing the component (A_2) with the other catalyst (1) or (2), may also be envisaged; depending on the configuration of the device, the components (A_1) and (A_2) may be distributed simultaneously or successively at the time of use.

In a third embodiment, the component (A) which is a single component or which includes two components (A_1) and (A_2) according to the invention may be in the form of one or two solid blocks that may be disintegrated in water, such as bath beads. The said solid blocks may be effervescent.

In the colouring agent in accordance with the invention, the colour fixing component (B) comprises an

aqueous composition containing at least one mineral or organic acid.

The pH of the component (B) generally ranges from 1 to 6 and more preferably from 2 to 5.

Among the mineral acids that may be used according to the invention, examples that may be mentioned include hydrochloric acid (HCl) and phosphoric acid (H_3PO_4), or mixtures thereof.

The compound (B) may consist of a naturally acidic water, for instance a demineralized water.

Among the organic acids that may be used according to the invention, mention may be made of acetic acid, α-hydroxy acids, β-hydroxy acids and α- and β-keto acids, and mixtures thereof.

The hydroxy acids are chosen especially from glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, mandelic acid and salicylic acid, and also alkyl derivatives thereof, for instance 5-n-octanoylsalicylic acid, 5-n-dodecanoylsalicylic acid or 2-hydroxy-3-methylbenzoic acid, or alternatively alkoxy derivatives thereof, for instance 2-hydroxy-3-methoxybenzoic acid, or mixtures thereof. Lactic acid, glycolic acid or citric acid and mixtures thereof will preferably be used according to the invention.

The colour fixing component (B) may be

packaged in various forms such as, especially, a bottle, a jar, a tube, sachets, wipes, an aerosol, a spray or a solid stick, or any other packaging form that is suitable for colouring the chosen keratin support.

According to the present invention, the component (C) for reviving the colour comprises an aqueous composition containing at least one mineral base and/or one organic base.

The pH of the component (B) generally ranges from 7 to 12 and more preferably from 8 to 10.

Among the mineral bases that may be used according to the invention, examples that may be mentioned include alkali metal or alkaline-earth metal salts, for instance sodium hydroxide, potassium hydroxide or aqueous ammonia; alkali metal and alkaline-earth metal hydrogen carbonates such as Na, K, Mg or Ca hydrogen carbonate and more particularly Na hydrogen carbonate; and mixtures thereof. The component (C) may also consist of a naturally alkaline mineral water such as Eau de Vichy or Eau de La Roche Posay.

Among the organic bases that may be mentioned, for example, are alkanolamines such as triethanolamine.

The component (C) for reviving the colour may be packaged in various forms such as a bottle, a jar, a

tube, sachets, wipes, an aerosol, a spray or a solid stick, or any other packaging form that is suitable for colouring the chosen keratin support.

To reveal the coloration of the compositions according to the invention, it suffices to place the composition containing at least one dye precursor and an effective amount of the catalytic system according to the invention in contact with an oxidizing medium such as a medium containing oxygen (for example atmospheric oxygen).

The compositions according to the invention are useful for colouring the human skin, scalp, nails or keratin fibres such as the hair, the eyelashes, the eyebrows and body hair. Various processes for applying the compositions according to the invention may be used.

According to a first colouring process, a single component (A) comprising at least one dye precursor and the catalytic system comprising the catalyst (1) and the catalyst (2) as defined above is applied to the keratin support in a first stage, in the presence of oxygen, for example atmospheric oxygen. When the desired shade is obtained, an acidic component (B) as defined above is applied to the keratin support to fix the colour. If it is desired to increase the intensity of the colour or to modify the shade, an

alkaline component (C) as defined above is then applied to the keratin support; the new colour obtained may be again fixed by means of a new application of the composition (B).

According to a second colouring process, a component (A_1) comprising at least one dye precursor and one of the catalysts (1) and (2) is applied to the keratin support in a first stage, and the colour is then revealed in the presence of oxygen, for example atmospheric oxygen, by applying a component (A_2) comprising the other catalyst (1) or (2) in a second stage. When the desired shade is obtained, an acidic component (B) as defined above is applied to the keratin support to fix the colour. If it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined above is applied to the keratin support; the new colour obtained may again be fixed by means of a new application of the composition (B).

According to a third colouring process, a single component (A) comprising at least one dye precursor and the catalytic system comprising the catalyst (1) and the catalyst (2) as defined above is applied to the keratin support in a first stage, in the presence of oxygen, for example atmospheric oxygen. If it is desired to increase the intensity of the colour

or to modify the shade, an alkaline component (C) as defined above is then applied to the keratin support; the new colour obtained may be fixed by applying the composition (B) as defined above.

According to a fourth colouring process, a component (A_1) comprising at least one dye precursor and one of the catalysts (1) and (2) is applied to the keratin support in a first stage, and the colour is then revealed in the presence of oxygen, for example atmospheric oxygen, by applying a component (A_2) comprising the other catalyst (1) or (2) in a second stage. If it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined above is applied to the keratin support; the new colour obtained may be fixed by applying the composition (B) as defined above.

Depending on the choice of dye precursors, the colouring agents of the invention may be used in many cosmetic applications. They may be used to dye the hair.

In the context of skin-specific cosmetics, the colouring agents of the invention may constitute compositions for artificially tanning and/or browning the skin, and/or for giving a healthy complexion.

In the context of skin-specific cosmetics, the colouring agents of the invention may constitute

skin makeup compositions especially for producing tattoos by means of stencils by adjusting the colours. They may also be used to adjust the colour according to the areas of relief of the face. They may be applied to the face or the hands to mask pigmentation defects such as vitiligo or a pregnancy mask, and also skin imperfections such as scars, age marks, chloasma and rosacea.

The colouring agents of the invention may constitute makeup compositions for the nails, the eyelashes and the eyebrows.

The colouring agents of the invention may constitute compositions for colouring keratinous textile fibres. The colouring agents of the invention may also be used for colouring food.

The examples that follow illustrate the present invention. In the examples, except where otherwise mentioned, all the percentages and parts are expressed on a weight basis.

Example 1

Component A containing the two components A_1 and A_2 below

Component A_1: White cream

Phase a_1:	Glyceryl stearate (and)	
	PEG-100 stearate	2.5%
	Polysorbate 60	2.5%

	Cetyl alcohol		1%
	Stearyl alcohol		1%
	Paraffin		5%
	Preserving agent		0.1%
Phase b_1:	Preserving agent		0.2%
	Carbomer		0.3%
	Base		0.2%
	Catechin		0.2%
	Propyl gallate		2%
	$MnCl_2$		0.0002%
	Water	qs	100%

Component A_2: White cream

Phase a_2:	Glyceryl stearate (and)		
	PEG-100 stearate		2.5%
	Polysorbate 60		2.5%
	Cetyl alcohol		1%
	Stearyl alcohol		1%
	Paraffin		5%
	Preserving agent		0.1%
Phase b_2:	Preserving agent		0.2%
	Carbomer		0.3%
	Sodium bicarbonate		1%
	Base		0.2%
	Water	qs	100%

Procedure:

Each phase a_1 or a_2 is prepared by homogenization of the various constituents at 75°C. Each phase b_1 or b_2 is added, respectively, to phase a_1 or a_2 at a temperature of 75°C. The mixture is cooled to 25°C.

Each of these preparations is introduced into one of the compartments of a two-compartment pump-dispenser bottle and will be mixed with the other preparation on exiting the pump, which will lead to the production of a tinted cream.

Component B: Acidic aqueous gel

Phase 1:	Acrylates/C_{10}-C_{30} alkyl acrylate crosspolymer		0.25%
	Base		0.15%
Phase 2:	Xanthan		0.3%
	Glycerol		3%
	Propylene glycol		3%
	PEG-8		3%
	Lactic acid		0.5%
	Preserving agent		0.1%
	Water	qs	100%

Procedure

Phase 1: The carboxylic acid is dispersed in the water and is then neutralized with the base.

Phase 2: The phase is prepared by homogenizing the various constituents. The mixing of phase 1 and phase 2 is then performed. The pH obtained is less than 5.

Compound C: Basic aqueous solution

Glycerol		3%
PEG-8		3%
Triethanolamine		0.9%
Preserving agent		0.1%
Eau de Vichy (Eau de Lucas)		5%
Water	qs	100%

The triethanolamine may advantageously be replaced with sodium hydroxide.

Component (A) is applied to the skin by means of the pump-dispenser bottle. A uniform colour is obtained after about 5 minutes, giving the user a tanned complexion. The colour thus obtained is then fixed by applying the acidic gel (B) to the coloured area of the skin. After a few hours, according to the wishes of the user, the colour may be revived (re-establish the first shade obtained by applying (A) and then (B)) by applying solution (C) optionally followed by applying product (B) to fix the colour again.

CLAIMS

1. Agent for colouring keratin materials, containing at least two components, characterized in that it comprises:

(i) a first component (A) by itself or including two components (A_1) and (A_2) comprising, in a physiologically acceptable medium, at least one dye precursor chosen from compounds comprising at least one aromatic ring containing at least two hydroxyl groups borne by two successive carbon atoms of the aromatic ring, and at least one catalytic system comprising a first catalyst (1) chosen from Mn(II) and/or Zn(II) salts and oxides, and mixtures thereof, and a second catalyst (2) chosen from alkali metal hydrogen carbonates and alkaline-earth metal hydrogen carbonates, and mixtures thereof; the catalysts (1) and (2) possibly being present in a single constituent or separated into two components (A_1) and (A_2);

(ii) a component (B) comprising an acidic composition, and/or

(iii) a component (C) comprising an alkaline composition.

2. Colouring agent according to Claim 1, in which the component (A) comprises two components (A1) and (A2), with:

(A1) comprising, in a physiologically acceptable

medium, the said dye precursor and one of the catalysts (1) or (2) and

(A2) comprising, in a physiologically acceptable medium, the other catalyst (1) or (2).

3. Colouring agent according to Claim 1 or 2, in which, in the component (A), the proportions of the first catalyst (1) and of the second catalyst (2) are chosen such that:

$$\frac{[Mn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \neq 0$$

$$\frac{[Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Zn(II)] \neq 0$$

$$\frac{[Mn(II)+Zn(II)]}{[HCO_3]} \leq 1 \text{ with } [Mn(II)] \text{ and } [Zn(II)] \neq 0$$

in which [Mn(II)], [Zn(II)] and $[HCO_3]$ represent, respectively, the molar concentrations of Mn(II), Zn(II) and HCO_3 in the composition.

4. Agent according to Claim 3, characterized in that the ratio $\frac{[Mn(II)]}{[HCO_3]}$ ranges from 10^{-5} to 10^{-1}, preferably from 10^{-3} to 10^{-2} and better still is about 5×10^{-3}.

5. Agent according to Claim 3 or 4, characterized in that the ratio $\frac{[Zn(II)]}{[HCO_3]}$ ranges from 10^{-4} to < 1, preferably from 10^{-3} to < 1 and better still

is about 5×10^{-1}.

6. Agent according to any one of Claims 3 to 5, characterized in that the ratio $\frac{[Mn(II)+Zn(II)]}{[HCO_3]}$ ranges from 10^{-5} to 10^{-1} and preferably from 10^{-3} to 10^{-2}.

7. Agent according to any one of Claims 1 to 6, characterized in that the Mn(II) and Zn(II) salts of the component (A) are chosen from the chloride, fluoride, iodide, sulfate, phosphate, nitrate and perchlorate, carboxylic acid salts, and mixtures thereof.

8. Agent according to Claim 7, characterized in that the Mn(II) and/or Zn(II) salt is the chloride.

9. Agent according to Claim 7, characterized in that the carboxylic acid salts are hydroxylated carboxylic acid salts.

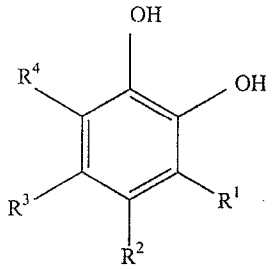
10. Agent according to Claim 9, characterized in that the hydroxylated carboxylic acid salt is the gluconate.

11. Agent according to any one of Claims 1 to 10, characterized in that the hydrogen carbonate is chosen from sodium hydrogen carbonate, potassium hydrogen carbonate, magnesium hydrogen carbonate and calcium hydrogen carbonate, and mixtures thereof.

12. Agent according to any one of Claims 1 to 11, characterized in that the aromatic ring

comprising at least two hydroxyl groups on two consecutive carbon atoms of the dye precursor is a benzene ring or a fused aromatic ring.

13. Agent according to Claim 12, characterized in that the dye precursor is a compound of formula:



(I)

in which the substituents R^1 to R^4, which may be identical or different, represent a hydrogen atom, a halogen, hydroxyl, carboxyl, alkylcarboxylate, optionally substituted amino, optionally substituted linear or branched alkyl, optionally substituted linear or branched alkenyl, optionally substituted cycloalkyl, alkoxy, alkoxyalkyl or alkoxyaryl radical, the aryl group possibly being optionally substituted, an aryl or substituted aryl radical, an optionally substituted heterocyclic radical, or a radical optionally containing one or more silicon atoms, in which two of the substituents R^1 to R^4 together form a saturated or unsaturated ring optionally containing one or more hetero atoms and optionally fused with one or more saturated or unsaturated rings optionally containing one or more hetero atoms.

14. Agent according to any one of Claims 1 to 13, characterized in that the dye precursor is chosen from flavanols, flavonols, anthocyanidins, anthocyanins, hydroxybenzoates, flavones and iridoids, these compounds possibly being osylated and/or in the form of oligomers, hydroxystilbenes which are optionally osylated, 3,4-dihydroxyphenylalanine and its derivatives, 2,3-dihydroxyphenylalanine and its derivatives, 4,5-dihydroxyphenylalanine and its derivatives, 4,5-dihydroxyindole and its derivatives, 5,6-dihydroxyindole and its derivatives, 6,7-dihydroxyindole and its derivatives, 2,3-dihydroxyindole and its derivatives, dihydroxycinnamates, hydroxycoumarins, hydroxyisocoumarins, hydroxycoumarones, hydroxyisocoumarones, hydroxychalcones, hydroxychromones, anthocyans, quinones and hydroxyxanthones, and mixtures of two or more of the above compounds.

15. Agent according to any one of Claims 1 to 14, characterized in that the dye precursor is chosen from extracts of plants, of fruits, of citrus plants and of vegetables, and mixtures thereof.

16. Agent according to Claim 15, characterized in that the dye precursor is chosen from extracts of tea, of grape, of apple, of cocoa, of

sorghum, of banana and of potato, and mixtures thereof.

17. Agent according to any one of Claims 1 to 16, characterized in that the dye precursor is present in the final component in (A) in an amount of at least 10 micromol per millilitre of component (A).

18. Agent according to any one of Claims 1 to 17, characterized in that the physiologically acceptable medium for the component (A) or for the components (A_1) and (A_2) is a solubilizing medium for the dye precursor, preferably with bacteriostatic properties.

19. Agent according to any one of Claims 1 to 18, characterized in that the physiologically acceptable medium for the component (A) or for the components (A_1) and (A_2) comprises a solvent or a mixture of solvents for the dye precursor.

20. Agent according to Claim 19, characterized in that the solvent is chosen from water, alcohols, ethers, dimethyl sulfoxide, N-methylpyrrolidone and acetones, and mixtures thereof.

21. Agent according to Claim 20, characterized in that the alcohol is an alkanol or an alkanediol.

22. Agent according to Claim 20, characterized in that the solvent is a water/alcohol mixture.

23. Agent according to Claim 22, characterized in that the alcohol represents up to 80% by weight of the mixture, preferably 1% to 50% by weight and better still from 5% to 20% by weight.

24. Agent according to any one of Claims 1 to 23, characterized in that the component (A) is free of any agent for chelating the Mn(II) and/or Zn(II) salt.

25. Colouring agent according to any one of Claims 1 to 23, in which the component (A) in the form of a single component or the components (A_1) and (A_2) are in the form of a cream, a milk, a gel, a cream-gel, a lotion, a powder or a solid block.

26. Colouring agent according to any one of Claims 1 to 24, in which the component (A) is packaged in a one-compartment device containing the dye precursor(s) and the catalytic system.

27. Colouring agent according to Claim 26, in which the device is chosen from the group consisting of an airtight metal tube, an ampule, a sachet, a sealed wipe, an aerosol containing one or more standard inert propellent gases, a pump device without air intake or a solid block.

28. Colouring agent according to any one of Claims 1 to 25, in which the component (A) including two components (A_1) and (A_2) is packaged in the form of

a kit comprising two separate containers; the first container containing the component (A_1) comprising the dye precursor(s) and one of the catalysts (1) or (2) as defined in the preceding claims, the other container containing the component (A_2) comprising the other catalyst (1) or (2), the components (A_1) and (A_2) being mixed together or applied successively at the time of use.

29. Colouring agent according to Claim 28, in which each container, independently of each other, is packaged in a device chosen from the group consisting of an airtight metal tube, an ampule, a sachet, a sealed wipe, an aerosol containing one or more standard inert propellent gases, a pump device without air intake or a solid block.

30. Colouring agent according to Claim 28, in which the device is a two-compartment aerosol containing, respectively, the components (A_1) and (A_2) and with which a distribution orifice may be selectively placed in communication; depending on the configuration of the device, the components (A_1) and (A_2) may be distributed simultaneously or successively at the time of use.

31. Colouring agent according to Claim 28, in which the device is a system containing two compartments each equipped with a pump without air

intake, the first compartment containing the component (A_1), and the other compartment containing the component (A_2); depending on the configuration of the device, the components (A_1) and (A_2) may be distributed simultaneously or successively at the time of use.

32. Colouring agent according to any one of Claims 1 to 23, in which the component (A) is in the form of one or two solid blocks that may be disintegrated in water.

33. Colouring agent according to any one of Claims 1 to 32, in which the component (B) comprises an aqueous composition containing at least one mineral or organic acid.

34. Colouring agent according to Claim 33, in which the pH of the component (B) generally ranges from 1 to 6 and more preferably from 2 to 5.

35. Colouring agent according to Claim 33, in which the mineral acid is chosen from hydrochloric acid (HCl) and phosphoric acid (H_3PO_4), or mixtures thereof.

36. Colouring agent according to Claim 33, in which the component (B) consists of a naturally acidic water.

37. Colouring agent according to Claim 33, in which the organic acid is chosen from acetic acid, α-hydroxy acids, β-hydroxy acids and α- and β-keto

acids, or mixtures thereof.

38. Colouring agent according to Claim 33, in which the organic acid is chosen from glycolic acid, lactic acid, malic acid, tartaric acid, citric acid, mandelic acid and salicylic acid, and also alkyl or alkoxy derivatives thereof, and mixtures thereof.

39. Colouring agent according to Claim 38, in which the organic acid is chosen from lactic acid, glycolic acid and citric acid, and mixtures thereof.

40. Colouring agent according to any one of Claims 1 to 39, in which the component (B) is packaged in the form of a bottle, a jar, a tube, a sachet, a wipe, an aerosol, a spray or a solid stick.

41. Colouring agent according to any one of Claims 1 to 40, in which the component (C) comprises an aqueous composition containing at least one mineral base and/or one organic base.

42. Colouring agent according to Claim 41, in which the pH of the component (C) generally ranges from 7 to 12 and more preferably from 8 to 10.

43. Colouring agent according to Claim 41, in which the mineral base is chosen from alkali metal and alkaline-earth metal salts and alkali metal and alkaline-earth metal hydrogen carbonates, and mixtures thereof.

44. Colouring agent according to Claim 41 or

42, in which the component (C) is a naturally alkaline mineral water.

45. Colouring agent according to Claim 41, in which the organic base is chosen from alkanolamines.

46. Colouring agent according to any one of Claims 1 to 45, in which the component (C) is packaged in the form of a bottle, a jar, a tube, a sachet, a wipe, an aerosol, a spray or a solid stick.

47. Process for colouring keratin materials, characterized in that a single component (A) comprising at least one dye precursor and the catalytic system comprising the catalyst (1) and the catalyst (2) as defined in any one of the preceding claims is applied to the keratin support in a first stage, in the presence of oxygen, for example atmospheric oxygen; when the desired shade is obtained, an acidic component (B) as defined in any one of the preceding claims is applied to the keratin support to fix the colour; if it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined in any one of the preceding claims is then applied to the keratin support; the new colour obtained may be again fixed by means of a new application of the composition (B).

48. Process for colouring keratin materials, characterized in that a component (A_1) comprising at

least one dye precursor and one of the catalysts (1) and (2) as defined in any one of the preceding claims is applied to the keratin support in a first stage, and the colour is then revealed in the presence of oxygen, for example atmospheric oxygen, by applying a component (A_2) comprising the other catalyst (1) or (2) in a second stage; when the desired shade is obtained, an acidic component (B) as defined in the preceding claims is applied to the keratin support to fix the colour. If it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined in any one of the preceding claims is applied to the keratin support; the new colour obtained may again be fixed by means of a new application of the composition (B).

49. Process for colouring keratin materials, characterized in that a single component (A) comprising at least one dye precursor and the catalytic system comprising the catalyst (1) and the catalyst (2) as defined in any one of the preceding claims is applied to the keratin support in a first stage, in the presence of oxygen, for example atmospheric oxygen; if it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined in any one of the preceding claims is then applied to the keratin support; the new colour obtained

may be fixed by applying the composition (B) as defined in any one of the preceding claims.

50. Process for colouring keratin materials, characterized in that a component (A_1) comprising at least one dye precursor and one of the catalysts (1) and (2) as defined in any one of the preceding claims is applied to the keratin support in a first stage, and the colour is then revealed in the presence of oxygen, for example atmospheric oxygen, by applying a component (A_2) comprising the other catalyst (1) or (2) in a second stage; if it is desired to increase the intensity of the colour or to modify the shade, an alkaline component (C) as defined in any one of the preceding claims is applied to the keratin support; the new colour obtained may be fixed by applying a composition (B) as defined in any one of the preceding claims.

51. Use of a colouring agent according to any one of Claims 1 to 46, as a hair colouring product.

52. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic product for artificially tanning and/or browning the skin, and/or for giving a healthy complexion.

53. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic skin makeup product.

54. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic product for camouflaging skin imperfections.

55. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic makeup product for the nails, the eyelashes and the eyebrows.

56. Use of a colouring agent according to any one of Claims 1 to 46, as a product for colouring keratinous textile fibres.

57. Use of a colouring agent according to any one of Claims 1 to 46, as a product for colouring food.

54. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic product for camouflaging skin imperfections.

55. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic makeup product for the nails, the eyelashes and the eyebrows.

56. Use of a colouring agent according to any one of Claims 1 to 46, as a product for colouring keratinous textile fibres.

55. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic product for camouflaging skin imperfections.

56. Use of a colouring agent according to any one of Claims 1 to 46, as a cosmetic makeup product for the nails, the eyelashes and the eyebrows.